Supporting Information for

Reusable Cyanide Sensing via Activation of C-H Group: Trifluoromethylcarbinol-directed meta-C-H Cyanomethylation of Naphthalimide

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1. $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR and HRMS-ESI spectrum of 2a

**Figure S1.** $^1$H-NMR (CDCl₃, 500 MHz) spectrum of compound 2a

**Figure S2.** $^{19}$F-NMR (CDCl₃, 470 MHz) spectrum of compound 2a
Figure S3. $^{13}$C-NMR (CDCl$_3$, 125 MHz) spectrum of compound 2a

Figure S4. HRMS-ESI mass spectrum of compound 2a
2. $^1$H-NMR, $^{13}$C-NMR and $^{19}$F-NMR spectrum of the mixture of isomers 3

Figure S5. $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of the mixture of cis-3 and trans-3 (1:0.7)

Figure S6. $^{19}$F-NMR (CDCl$_3$, 470 MHz) spectrum of the mixture of cis-3 and trans-3 (1:0.7)
Figure S7. $^{13}$C-NMR (CDCl$_3$, 125 MHz) spectrum of the mixture of cis-3 and trans-3 (1:0.7)

3. $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR and HRMS-ESI spectrum of cis-3 and trans-3

Figure S8. $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of compound cis-3
Figure S9. $^{19}$F-NMR (CDCl$_3$, 470 MHz) spectrum of compound cis-3

Figure S10. $^{13}$C-NMR (CDCl$_3$, 125 MHz) spectrum of compound cis-3
Figure S11. HRMS-ESI mass spectrum of compound *cis*-3

Figure S12. $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of compound *trans*-3
Figure S13. $^{19}$F-NMR (CDCl$_3$, 470 MHz) spectrum of compound $trans$-3

Figure S14. $^{13}$C-NMR (CDCl$_3$, 125 MHz) spectrum of compound $trans$-3
Figure S15. HRMS-ESI mass spectrum of compound trans-3

4. $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR and HRMS-ESI spectrum of 2b and 4

Figure S16. $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of compound 2b
Figure S17. $^{13}$C-NMR (CDCl₃, 125 MHz) spectrum of compound 2b

Figure S18. HRMS-ESI mass spectrum of compound 2b
Figure S19. $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of compound 4

Figure S20. $^{13}$C-NMR (CDCl$_3$, 125 MHz) spectrum of compound 4
Figure S21. HRMS-ESI mass spectrum of compound 4

5. Molecular modeling calculations for 2a, cis-3, deprotonation of cis-3

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Figure S22. Equilibrium structure calculation of 2 (a) Face-on and (b) edge-on views; cis-3 (c) Face-on and (d) edge-on views; deprotonation of cis-3 (e) Face-on and (f) edge-on views.
6. UV-vis titration of cis-3 with $F^-$ and selective testing in CH$_3$CN

**Figure S23.** (a) UV-visible titration of cis-3 (20 μM) with TBAF (0 to 2.7 equiv.) in CH$_3$CN. The inset shows the absorbance at 550 nm as a function of [F$^-$]; (b) UV-visible spectra of cis-3 (20 μM) in the presence of different anions (ca.1.6 equiv) in CH$_3$CN; Inset: Color change of cis-3 with different anions (from left to right: cis-3 only, CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$).

7. UV-vis interference experiments of cis-3 toward CN$^-$ in CH$_3$CN and CH$_3$CN-H$_2$O

**Figure S24.** (a) Interference experiments of cis-3 (20 μM) in CH$_3$CN for CN$^-$ in the presence of other anions. The gray bars represent the emission at 550 nm of cis-3 in the presence of 1.6 equiv. of the anion of interest (from 0 to 9: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$). The red bars indicate the change that occurs upon subsequent addition of 1.6 equiv. of CN$^-$ to the solution containing cis-3 and the anion of interest; (b) Interference experiments of cis-3 (20 μM) in CH$_3$CN/H$_2$O (9:1, v/v) for CN$^-$ in the presence of other anions. The gray bars represent the emission at 545 nm of cis-3 in the presence of 80.0 equiv. of the anion of interest (from 0 to 9: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$, S$^{2-}$, SCN$^-$). The red bars indicate the change that occurs upon subsequent addition of 80.0 equiv. of CN$^-$ to the solution containing cis-3 and the anion of interest.
8. Influence of pH on the absorbance of cis-3 in CH₃CN-H₂O

**Figure S25.** Influence of pH on the absorbance at 550 nm of cis-3 and cis-3+CN⁻ in CH₃CN/H₂O (9:1, v/v).

9. Emission spectra of titration of cis-3 with CN⁻ and selective testing in CH₃CN

**Figure S26.** (a) Emission spectra of cis-3 (20 μM, λₑₓ = 337 nm, in CH₃CN) upon addition of increasing concentrations of CN⁻ (as its TBA salt, 0 to 1.8 equiv). Inset: Plot of emission intensity (λₑₘ = 378 nm) versus TBACN concentration; (b) Fluorescence spectra of cis-3 (20 μM) in the presence of different anions (CN⁻, F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, H₂PO₄⁻, AcO⁻, BF₄⁻, NO₃⁻, ClO₄⁻) (ca. 1.8 equiv.) in CH₃CN.

10. Emission interference experiments of cis-3 toward CN⁻ in CH₃CN and CH₃CN-H₂O
**Figure S27.** (a) Fluorescence spectra of probe *cis*-3 (20 μM) in presence of various anion (1.8 equiv.) in CH$_3$CN solution. The gray bars represent the emission at 378 nm in the presence of 1.8 equiv. of the anion of interest (form 0 to 9: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$). The red bars indicate the change that occurs upon subsequent addition of 1.8 equiv. of CN$^-$ to the solution containing *cis*-3 and the anion of interest; (b) Fluorescence spectra of probe *cis*-3 (20 μM) in presence of various anion (90.0 equiv.) in CH$_3$CN solution. The gray bars represent the emission at 388 nm in the presence of 90.0 equiv. of the anion of interest (form 0 to 11: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$, S$^{2-}$, SCN$^-$). The red bars indicate the change that occurs upon subsequent addition of 90.0 equiv. of CN$^-$ to the solution containing *cis*-3 and the anion of interest.

11. **The fluorescence detection limit of *cis*-3 with CN$^-$ in CH$_3$CN-H$_2$O solution.**

![](FigureS28.png)

**Figure S28.** Emission intensity ratio (F$_{488}$) of *cis*-3 (20 μM) as a function of CN$^-$ concentration from 0-1800 μM (0–90 equiv) in CH$_3$CN/H$_2$O (9:1, v/v).

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<th>Error</th>
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<tr>
<td>B</td>
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<tr>
<td>R</td>
<td>SD</td>
<td>N</td>
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The result of the analysis as follows:

Linear Equation: \( Y = -1.99227 + 0.17447 \times X, \quad R^2 = 0.94957 \)

\( S = 0.17447 \times 10^4, \quad K = 3, \quad \delta = 0.0.03218 \)

\[ \text{LOD} = K \times \delta / S = 0.553 \mu M \]

**12. Molecular modeling calculations for trans-3**

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**13. UV-vis absorbance spectra of trans-3**

**Figure S29.** Equilibrium structure calculation of trans-3 (a) Face-on and (b) edge-on views.

**Figure S30.** (a) UV-visible titration of trans-3 (20 μM) with TBACN (0 to 1.2 equiv.) in CH₂CN. The inset shows the absorbance at 569 nm as a function of CN⁻; (b) UV-visible spectra of trans-3 (20 μM) in the presence of different anions (ca.1.2 equiv) in CH₂CN; Inset: Color change of trans-3 with different anions (from left to right: trans-3 only, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, H₂PO₄⁻, AcO⁻, BF₄⁻, NO₃⁻, ClO₄⁻).
**Figure S31.** (a) UV-visible titration of trans-3 (20 μM) with TBACN (0 to 100.0 equiv.) in CH$_3$CN/H$_2$O (9:1, v/v). The inset shows the absorbance at 559 nm as a function of CN$^-$. (b) UV-visible spectra of trans-3 (20 μM) in the presence of different anions (ca.100.0 equiv) in CH$_3$CN/H$_2$O (9:1, v/v); Inset: Color change of trans-3 with different anions (from left to right: trans-3 only, CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_3$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$, S$^{2-}$, SCN$^-$).

**Figure S32.** (a) Interference experiments of trans-3 (20 μM) in CH$_3$CN for CN$^-$ in the presence of other anions. The gray bars represent the emission at 569 nm of trans-3 in the presence of 1.2 equiv. of the anion of interest (from 0 to 9: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_3$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$). The red bars indicate the change that occurs upon subsequent addition of 1.2 equiv. of CN$^-$ to the solution containing trans-3 and the anion of interest; (b) Interference experiments of trans-3 (20 μM) in CH$_3$CN/H$_2$O (9:1, v/v) for CN$^-$ in the presence of other anions. The gray bars represent the emission at 559 nm of trans-3 in the presence of 100.0 equiv. of the anion of interest (from 0 to 9: F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_3$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$, S$^{2-}$, SCN$^-$). The red bars indicate the change that occurs upon subsequent addition of 100.0 equiv. of CN$^-$ to the solution containing trans-3 and the anion of interest.
Figure S33. UV-visible titration of *trans*-3+CN⁻ (20 μM) with TFA (0 to 1.2 equiv.) in CH₃CN. The inset shows the absorbance at 569 nm as a function of TFA.

Figure S34. (a) Relative UV-visible absorbance during the titration of *trans*-3 with CN⁻ and H⁺ (TFA) in CH₃CN; (b) visual color after each sequential addition of CN⁻ and H⁺ (TFA) in CH₃CN.
Figure S35. Influence of pH on the absorbance at 559 nm of trans-3 and trans-3$+$CN$^-$ in CH$_3$CN/H$_2$O (9:1, v/v).

14. Fluorescence emission spectra of trans-3

Figure S36. (a) Emission spectra of trans-3 (20 $\mu$M, $\lambda_{ex}$ = 335 nm, in CH$_3$CN) upon addition of increasing concentrations of CN$^-$ (as its TBA salt, 0 to 1.4 equiv). Inset: Plot of emission intensity ($\lambda_{em}$ = 382 nm) versus TBACN concentration; (b) Fluorescence spectra of trans-3 (20 $\mu$M) in the presence of different anions (CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$) (ca. 1.4 equiv) in CH$_3$CN.

Figure S37. (a) Emission spectra of trans-3 (20 $\mu$M, $\lambda_{ex}$ = 335 nm, in CH$_3$CN/H$_2$O (9:1, v/v)) upon addition of increasing concentrations of CN$^-$ (as its TBA salt, 0 to 120.0 equiv). Inset: Plot of emission intensity ($\lambda_{em}$ = 382 nm) versus TBACN concentration; (b) Fluorescence spectra of trans-3 (20 $\mu$M) in the presence of different anions (CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, BF$_4^-$, NO$_3^-$, ClO$_4^-$, S$^2^-$, SCN$^-$) (ca. 120.0 equiv) in CH$_3$CN/H$_2$O (9:1, v/v).
**Figure S38.** (a) Fluorescence spectra of probe \( \text{trans-3} \) (20 \( \mu \)M) in presence of various anion (1.4 equiv.) in CH\(_3\)CN solution. The gray bars represent the emission at 382 nm in the presence of 1.4 equiv. of the anion of interest (form 0 to 9: \( F^- \), \( Cl^- \), \( Br^- \), \( I^- \), \( HSO_4^- \), \( H_2PO_4^- \), \( AcO^- \), \( BF_4^- \), \( NO_3^- \), \( ClO_4^- \)). The red bars indicate the change that occurs upon subsequent addition of 1.4 equiv. of CN\(^-\) to the solution containing \( \text{trans-3} \) and the anion of interest; (b) Fluorescence spectra of probe \( \text{trans-3} \) (20 \( \mu \)M) in presence of various anion (120.0 equiv.) in CH\(_3\)CN/H\(_2\)O (9:1, v/v) solution. The gray bars represent the emission at 382 nm in the presence of 120.0 equiv. of the anion of interest (form 0 to 11: \( F^- \), \( Cl^- \), \( Br^- \), \( I^- \), \( HSO_4^- \), \( H_2PO_4^- \), \( AcO^- \), \( BF_4^- \), \( NO_3^- \), \( ClO_4^- \), \( S^{2-} \), \( SCN^- \)). The red bars indicate the change that occurs upon subsequent addition of 120.0 equiv. of CN\(^-\) to the solution containing \( \text{trans-3} \) and the anion of interest.